

FORM-PTO-1390
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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

003277-032

APPLICATION NO. (If known, use 37 C.F.R. 1.5)

10/018087

INTERNATIONAL APPLICATION NO.
PCT/FI00/00534

INTERNATIONAL FILING DATE
14 June 2000

PRIORITY DATE CLAIMED
25 June 1999

TITLE OF INVENTION

BLEACHING ACTIVATOR AND PROCESS FOR USING ACTIVATOR

APPLICANT(S) FOR DO/EO/US

1) Jukka JÄKÄRÄ; and 2) Aarto PARÉN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☒ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

International Search Report, International Preliminary Examination Report, Written Opinion, Form PCT/IB/304, PCT/IB/308, and Marked-up copy of Substitute Specification



21839

U.S. APPLICATION NO. (If known, enter 37 CFR 1.101) 107018087		INTERNATIONAL APPLICATION NO. PCT/FI00/00534		ATTORNEY'S DOCKET NUMBER 003277-032	
21. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)):					
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,040.00 (960)					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 (970)					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 (958)					
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 (956)					
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962)					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 1,040.00	
Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$ --	
Claims	Number Filed	Number Extra	Rate		
Total Claims	10 -20 =	0	X\$18.00 (966)	\$ 0.00	
Independent Claims	3 -3 =	0	X\$84.00 (964)	\$ 0.00	
Multiple dependent claim(s) (if applicable)				+ \$280.00 (968)	\$ --
TOTAL OF ABOVE CALCULATIONS =				\$ 1,040.00	
Reduction for 1/2 for filing by small entity, if applicable (see below).				+	\$ --
SUBTOTAL =				\$ 1,040.00	
Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$ --	
TOTAL NATIONAL FEE =				\$ 1,040.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property				+	\$ --
TOTAL FEES ENCLOSED =				\$ 1,040.00	
				Amount to be refunded:	\$
				charged:	\$
<p>a. <input type="checkbox"/> Small entity status is hereby claimed.</p> <p>b. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1,040.00</u> to cover the above fees is enclosed.</p> <p>c. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u>. A duplicate copy of this sheet is enclosed.</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO:</p> <p>Ronald L. Grudziecki BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620</p> <div style="text-align: right; margin-top: 20px;"> SIGNATURE <u>Scott W. Cummings</u> NAME 41,567 REGISTRATION NUMBER December 14, 2001 DATE </div>					

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of) BOX PCT/US
)
Jukka JÄKÄRÄ et al.)
)
Application No.: [Not Assigned])
International Application PCT/FI00/00534)
)
I.A. Date: June 14, 2000)
)
For: BLEACHING ACTIVATOR AND)
PROCESS FOR USING ACTIVATOR)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application on the merits, please amend the application as follows.

IN THE SPECIFICATION:

After the last page of the specification, please add the Abstract attached hereto as a separate sheet.

Also, please enter the attached Substitute Specification pursuant to 37 C.F.R. §1.125.

IN THE CLAIMS:

Please replace claims 1-10 with the corresponding amended claims.

1. (Amended) A peroxide bleaching solution for bleaching paper pulp containing lignin, the solution comprising: a bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol.

2. (Amended) The peroxide bleaching solution according to Claim 1, wherein the activator is glycerol triacetate.

3. (Amended) The peroxide bleaching solution according to Claim 1, wherein the activator is glycerol diacetate.

4. (Amended) The peroxide bleaching solution according to Claim 1, wherein the bleaching solution additionally comprises a chelating agent, a stabilizer, lye, and waterglass.

5. (Amended) The peroxide bleaching solution according to Claim 1, wherein the bleaching solution comprises peracetic acid.

6. (Amended) A method of bleaching of paper pulp containing lignin to improve opacity comprising adding mono-, di- or triformic, acetic or propionic ester of glycerol as a bleaching activator in peroxide to the paper pulp.

7. (Amended) A method for bleaching pulp containing lignin with a bleaching solution containing hydrogen peroxide, comprising adding a bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol to the bleaching solution to improve the opacity.

8. (Amended) The method according to Claim 7, wherein the pulp to be bleached comprises a mechanical pulp.

9. (Amended) The method according to Claim 7, wherein the activator is added in amount of 0.2-5 kg/ton of pulp.

10. (Amended) The method according to Claim 7, wherein the activator is added in amount of 1-3 kg/ton of pulp.

REMARKS

By way of the foregoing amendments, the specification and claims have been amended to place them in better form for examination. No new matter has been added.

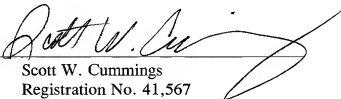
A Substitute Specification is being submitted to make minor changes. No new matter has been introduced.

Also enclosed is a version of the Substitute Specification in which the amendments are shown with bracketing and underlining.

Early and favorable consideration with respect to this application is respectfully requested. Should any questions arise in connection with this application, the undersigned respectfully requests that he be contacted at the number indicated below.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 
Scott W. Cummings
Registration No. 41,567

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Date: December 14, 2001

003277-032602

Attachment to Preliminary Amendment dated December 14, 2001

Marked-up Claims 1-10

1. (Amended) A peroxide bleaching solution for bleaching [activator for use in] paper pulp containing lignin, the solution comprising: a bleaching activator comprising [characterized in that the activator is] a mono-, di- or triformic, acetic or propionic ester of glycerol.

2. (Amended) [A] The peroxide bleaching [activator] solution according to Claim 1, [characterized in that] wherein the activator is glycerol triacetate.

3. (Amended) [A] The peroxide bleaching [activator] solution according to Claim 1, [characterized in that] wherein the activator is glycerol diacetate.

4. (Amended) [A] The peroxide bleaching [activator] solution according to Claim 1, [characterized in that] wherein the [activator is used in peroxide bleaching of chemical or mechanical pulp] bleaching solution additional comprises a chelating agent, a stabilizer, lye, and waterglass.

5. (Amended) [A] The peroxide bleaching [activator] solution according to Claim 1, [characterized in that the amount of the activator used is 0.2 – 5kg/ton of pulp] wherein the bleaching solution comprises peracetic acid.

Attachment to Preliminary Amendment dated December 14, 2001

Marked-up Claims 1-10

6. (Amended) A method of bleaching of paper pulp containing lignin to improve opacity comprising adding mono-, di- or triformic, acetic or propionic ester of glycerol as a bleaching activator in peroxide to the paper [according to Claim 1, characterized in that the amount of the activator used is 1 – 3kg/ton of] pulp.

7. (Amended) A method for bleaching pulp containing lignin with a [activator according to Claim 1, characterized in that the] bleaching solution containing [the activator also contains chelating agents, stabilizers, lye, and waterglass] hydrogen peroxide, comprising adding a bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol to the bleaching solution to improve the opacity.

8. (Amended) [A] The method [bleaching activator] according to Claim 1, characterized in that the activator is used together with peracetic acid] 7, wherein the pulp to be bleached comprises a mechanical pulp.

9. (Amended) The [use of mono-, di- or triformic, acetic or propionic ester of glycerol as a bleaching activator in paper pulp containing lignin] method according to Claim 7, wherein the activator is added in amount of 0.2-5 kg/ton of pulp.

Attachment to Preliminary Amendment dated December 14, 2001

Marked-up Claims 1-10

10. (Amended) [A bleaching method for pulp containing lignin, characterized in that an activator according to Claim 1 is added to a bleaching solution containing hydrogen peroxide to improve the opacity] The method according to Claim 7, wherein the activator is added in amount of 1-3 kg/ton of pulp.

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**BLEACHING ACTIVATOR AND
PROCESS FOR USING THE ACTIVATOR**

FIELD OF THE INVENTION

[0001] The invention relates to a bleaching activator for improving the opacity of bleached pulps containing lignin, and to a method for using the activator.

BACKGROUND OF THE INVENTION

[0002] In the description of the background of the present invention that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art with regard to the present invention.

[0003] Opacity is used to describe the nontransparent aspect of paper, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the

pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

[0004] Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide, which works as the actual bleaching agent, is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide.

[0005] We have observed that peracetic acid treatment, for example, can provide a clearly higher opacity with the same level of brightness than when pulp is bleached with hydrogen peroxide alone.

[0006] Peracetic acid can also be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before use, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching

solution ($\text{NaOH} + \text{H}_2\text{O}_2 + \text{waterglass}$), it would readily cause silicate precipitate and consume the lye.

[0007] Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP Application 284598). However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

[0008] A technically useful activator should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the alkaline peroxide bleaching. Because of environmental matters, a nitrogen-free activator would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, an activator should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a registered, reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the peroxide bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

SUMMARY OF THE INVENTION

[0009] The purpose of this invention is to find a useful activator that is used in pulp bleaching and that fulfills the conditions mentioned above.

[0010] According to one aspect, the present invention provides a peroxide bleaching solution for bleaching paper pulp comprising: lignin, and a bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol.

BRIEF DESCRIPTION OF THE DRAWING

[0011] Fig. 1 is a plot showing brightness vs. opacity when peroxide is used to bleach pulp.

DETAILED DESCRIPTION OF THE INVENTION

[0012] According to the invention, we have surprisingly observed that carboxylic acid esters of glycerol known per se are very suitable to be used as activator agents. From the point of view of industrial hygiene, the carboxylic acid esters of glycerol are almost harmless. Useful carboxylic esters of glycerol include the monoesters, diesters, and triesters of formic acid, acetic acid, and propionic acid in particular. Especially preferable activator agents to be added to the bleaching process comprise acetic esters of glycerol, such as triacetine and diacetine. Even if these esters as such were not water soluble, they dissolve completely in an alkaline peroxide solution, because the acetyl groups split off producing percarboxylic acid in situ. Glycerol and carboxylic acid are the residues of the chemical. By default, bleaching produces glycerol and acetic acid.

[0013] Activators according to the invention include mono-, di- and triformic, acetic and propionic esters of glycerol. Mono-, di- and triacetic esters of glycerol are preferable.

[0014] As it is assumed that the generation of peracid in peroxide bleaching is the reaction mechanism of the activator, the excess length of the hydrocarbon chain reduces the effect of the activator. When the hydrocarbon chain increases, a smaller amount of peracid is obtained as the amount of material than with shorter hydrocarbon chains.

[0015] A suitable dose of the activator has been found to be 0.2–5 kg/ton of pulp. A preferable dosage is 1–3 kg/ton of pulp. The bleaching conditions can be normal; in bleaching mechanical pulps, for example, we have used a temperature of 50–90°C, a consistency of 5–40%, and a retention of 30–240 min. Depending on the level of brightness, the dose of peroxide may vary within 5–50 kg/ton of pulp. Correspondingly, the doses of lye and waterglass must be adjusted to be suitable for the dose of peroxide. In addition to lye, waterglass, and hydrogen peroxide, the bleaching solution can contain a chelating agent, such as DTPA or some other stabilizers. The activators are suitable to be used for bleaching mechanical pulps in particular, such as ground wood (SGW, PGW), refiner mechanical pulp (TMP) or chemi-mechanical pulps (CTMP). Activators can also be used in the peroxide bleaching of chemical pulps, such as sulphate and sulphite pulp. The sort of wood used for the manufacture of pulp has no significance for the functioning of the invention.

[0016] In the following, the invention is described mainly with the aid of

Examples 1 to 4.

Example 1

[0017] Chemi-mechanical pulp (CTMP) was treated with peroxide in a normal manner. The effect of the bleaching activator is shown in Table 1.

Table 1

[0018] CTMP, bleaching solution: 24 kg of NaOH + 20 kg of waterglass + 30 kg/ton of pulp of H_2O_2
t = 70°C, consistency 30%, 120 min, chelated pulp

Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Yellowness	Opacity
None	-	78.4	17.7	64.9
PAA	2	79.1	17	67.2
Triacetine	5	78	17.9	67.2
Triacetine	2	78.3	17.8	68.6

[0019] The results indicate that by adding the activator to the peroxide bleaching, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone. The results also show that the activators had hardly any effect on the ISO brightness.

Example 2

[0020] Refiner mechanical pulp of spruce with a brightness of 60.4% ISO, opacity of 86.5, containing 100 ppm of Mn and 18 ppm of Fe, was brought to peroxide bleaching. The results are in Table 2.

Table 2 TMP (spruce), bleaching stages

[0021] Chelating treatment: Consistency 10%, pH 5.5, 45 min, t = 55°C, 2 kg/ton of pulp of DTPA

Consistency to 15%

Peroxide bleaching: 120 min, t = 70°C, consistency 15%, 22 kg of H₂O₂, 22 kg of NaOH, 17.6 kg/ton of pulp of waterglass

Activator	Dosage kg/ton of pulp	H ₂ O ₂ residue, kg/ton of pulp	Brightness, % ISO	Opacity, %
None	0	9.2	74.5	81.4
Triacetine	1	9.4	75.8	83.1
Triacetine	2	9.9	75.5	82.8

[0022] The results show that the activator in peroxide bleaching obviously had a positive effect on the opacity of the pulp, when compared with peroxide bleaching without the added activator.

Example 3

[0023] Pressure groundwood pulp was treated with peroxide in a normal manner.

The effect of the bleaching activator is shown in Table 3.

Table 3 PGW (pressure groundwood pulp)

[0024] Peroxide bleaching: Consistency 28%, 120min, $t = 70^{\circ}\text{C}$, 25 kg of H_2O_2 , 18.8 kg of waterglass, 25 kg of NaOH, chelated at the plant

Triacetine, kg/ton of pulp	Brightness, % ISO	Opacity, %	Light scattering	Light absorption
0	77.5	86.4	67.4	0.37
1	77.8	87.8	70.3	0.36
2	77.8	88.6	73.9	0.37

Example 4

[0025] Mechanical pulp was treated with peroxide in a normal manner. The effect of the bleaching activator in peroxide bleaching is shown in Table 4.

Table 4

[0026] TMP, bleaching solution: 20 kg of NaOH + 18.8 kg of waterglass + 20 kg of H_2O_2 , 2 kg of DTPA
 $t = 70^{\circ}\text{C}$, consistency 28%, 120 min, plant-chelated pulp

Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	77.8	79.4
Triacetine	1	77.9	81.3
Triacetine	2	77.8	81.1
Triacetine	5	77.5	81.7
Diacetine	2	77.8	81.5

[0027] The results show that the activator had a distinct effect on the opacity with the same level of brightness as peroxide bleaching alone. We can also observe that the activators have no effect on the ISO brightness.

[0028] While the present invention has been described by reference to the above-mentioned embodiments, certain modifications and variations will be evident to those of ordinary skill in the art. Therefore, the present invention is limited only by the scope and spirit of the appended claims.

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[Bleaching activator and process for using the activator]
BLEACHING ACTIVATOR AND
PROCESS FOR USING THE ACTIVATOR

FIELD OF THE INVENTION

[0001] The invention relates to a bleaching activator for improving the opacity of bleached pulps containing lignin, and to a method for using the activator.

BACKGROUND OF THE INVENTION

[0002] In the description of the background of the present invention that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art with regard to the present invention.

[0003] Opacity is used to describe the nontransparent aspect of paper, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the

pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

[0004] Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide, which works as the actual bleaching agent, is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide.

[0005] We have observed that peracetic acid treatment, for example, can provide a clearly higher opacity with the same level of brightness than when pulp is bleached with hydrogen peroxide alone.

[0006] Peracetic acid can also be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before use, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching

solution ($\text{NaOH} + \text{H}_2\text{O}_2 + \text{waterglass}$), it would readily cause silicate precipitate and consume the lye.

5 [0007] Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP [application] Application 284598). However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

10 [0008] A technically useful activator should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the alkaline peroxide bleaching. Because of environmental matters, a nitrogen-free activator would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, an activator should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a registered, reasonable, commercial chemical that is easy to get and can be added
15 to the pulp as early as at the peroxide bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

SUMMARY OF THE INVENTION

20 [0009] The purpose of this invention is to find a useful activator that is used in pulp bleaching and that [fulfils] fulfills the conditions mentioned above.
[The main features of the invention are disclosed by the appended Claims.]

[0010] According to one aspect, the present invention provides a peroxide bleaching solution for bleaching paper pulp comprising: lignin, and a bleaching activator comprising a mono-, di- or triformic, acetic or propionic ester of glycerol.

BRIEF DESCRIPTION OF THE DRAWING

[0011] Fig. 1 is a plot showing brightness vs. opacity when peroxide is used to bleach pulp.

DETAILED DESCRIPTION OF THE INVENTION

[0012] According to the invention, we have surprisingly observed that carboxylic acid esters of glycerol known per se are very suitable to be used as activator agents. From the point of view of industrial hygiene, the carboxylic acid esters of glycerol are almost harmless. Useful carboxylic esters of glycerol include the monoesters, diesters, and triesters of formic acid, acetic acid, and propionic acid in particular. Especially preferable activator agents to be added to the bleaching process comprise acetic esters of glycerol, such as triacetine and diacetine. Even if these esters as such were not water soluble, they dissolve completely in an alkaline peroxide solution, because the acetyl groups split off producing percarboxylic acid in situ. Glycerol and carboxylic acid are the residues of the chemical. By default, bleaching produces glycerol and acetic acid.

[0013] Activators according to the invention include mono-, di- and triformic, acetic and propionic esters of glycerol. Mono-, di- and triacetic esters of glycerol are preferable.

[0014] As it is assumed that the generation of peracid in peroxide bleaching is the reaction mechanism of the activator, the excess length of the hydrocarbon chain reduces the effect of the activator. When the hydrocarbon chain increases, a smaller amount of peracid is obtained as the amount of material than with shorter hydrocarbon chains.

[0015] A suitable dose of the activator has been found to be 0.2–5 kg/ton of pulp. A preferable dosage is 1–3 kg/ton of pulp. The bleaching conditions can be normal; in bleaching mechanical pulps, for example, we have used a temperature of 50–90°C, a consistency of 5–40%, and a retention of 30–240 min. Depending on the level of brightness, the dose of peroxide may vary within 5–50 kg/ton of pulp. Correspondingly, the doses of lye and waterglass must be adjusted to be suitable for the dose of peroxide. In addition to lye, waterglass, and hydrogen peroxide, the bleaching solution can contain a chelating agent, such as DTPA or some other stabilizers. The activators are suitable to be used for bleaching mechanical pulps in particular, such as ground wood (SGW, PGW), refiner mechanical pulp (TMP) or chemi-mechanical pulps (CTMP). Activators can also be used in the peroxide bleaching of chemical pulps, such as sulphate and sulphite pulp. The sort of wood used for the manufacture of pulp has no significance for the functioning of the invention.

[0016] In the following, the invention is described mainly with the aid of
[examples] Examples 1 to 4.

Example 1

[0017] Chemi-mechanical pulp (CTMP) was treated with peroxide in a normal
manner. The effect of the bleaching activator is shown in Table 1.

Table 1

[0018] CTMP, bleaching solution: 24 kg of NaOH + 20 kg of waterglass + 30
kg/ton of pulp of H_2O_2
t = 70°C, consistency 30%, 120 min, chelated pulp

Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Yellowness	Opacity
None	-	78.4	17.7	64.9
PAA	2	79.1	17	67.2
Triacetine	5	78	17.9	67.2
Triacetine	2	78.3	17.8	68.6

[0019] The results indicate that by adding the activator to the peroxide bleaching,
a distinctly higher opacity with the same brightness level is achieved than by using
peroxide bleaching alone. The results also show that the activators had hardly any
effect on the ISO brightness.

Example 2

[0020] Refiner mechanical pulp of spruce with a brightness of 60.4 % ISO, opacity of 86.5, containing 100 ppm of Mn and 18 ppm of Fe, was brought to peroxide bleaching. The results are in Table 2.

Table 2 TMP (spruce), bleaching stages

[0021] Chelating treatment: Consistency 10 %, pH 5.5, 45 min, $t = 55^{\circ}\text{C}$, 2 kg/ton of pulp of DTPA

Consistency to 15 %

Peroxide bleaching: 120 min, $t = 70^{\circ}\text{C}$, consistency 15 %, 22 kg of H_2O_2 , 22 kg of NaOH, 17.6 kg/ton of pulp of waterglass

Activator	Dosage kg/ton of pulp	H_2O_2 residue, kg/ton of pulp	Brightness, % ISO	Opacity, %
None	0	9.2	74.5	81.4
Triacetine	1	9.4	75.8	83.1
Triacetine	2	9.9	75.5	82.8

[0022] The results show that the activator in peroxide bleaching obviously had a positive effect on the opacity of the pulp, when compared with peroxide bleaching without the added activator.

Example 3

[0023] Pressure groundwood pulp was treated with peroxide in a normal manner.

The effect of the bleaching activator is shown in Table 3.

Table 3 PGW (pressure groundwood pulp)

[0024] Peroxide bleaching: Consistency 28%, [12 0min] 120min, $t = 70^{\circ}\text{C}$, 25 kg of H_2O_2 , 18.8 kg of waterglass, 25 kg of NaOH, chelated at the plant

Triacetine, kg/ton of pulp	Brightness, % ISO	Opacity, %	Light scattering	Light absorption
0	77.5	86.4	67.4	0.37
1	77.8	87.8	70.3	0.36
2	77.8	88.6	73.9	0.37

Example 4

[0025] Mechanical pulp was treated with peroxide in a normal manner. The effect of the bleaching activator in peroxide bleaching is shown in Table 4.

Table 4

[0026] TMP, bleaching solution: 20 kg of NaOH + 18.8 kg of waterglass + 20 kg of H_2O_2 , 2 kg of DTPA
 $t = 70^{\circ}\text{C}$, consistency 28%, 120 min, plant-chelated pulp

Activator	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	77.8	79.4
Triacetine	1	77.9	81.3
Triacetine	2	77.8	81.1
Triacetine	5	77.5	81.7
Diacetine	2	77.8	81.5

[0027] The results show that the activator had a distinct effect on the opacity with the same level of brightness as peroxide bleaching alone. We can also observe that the activators have no effect on the ISO brightness.

[0028] While the present invention has been described by reference to the above-mentioned embodiments, certain modifications and variations will be evident to those of ordinary skill in the art. Therefore, the present invention is limited only by the scope and spirit of the appended claims.

202507-032001

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

003277-032

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

BLEACHING ACTIVATOR AND PROCESS FOR USING THE ACTIVATOR

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FI00/00534

on 14 June 2000

and was amended

on 23 May 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations. §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
Finland	991365	15 June 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
PCT	PCT/FI00/534	14 June 2000	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
 (Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

003277-032

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